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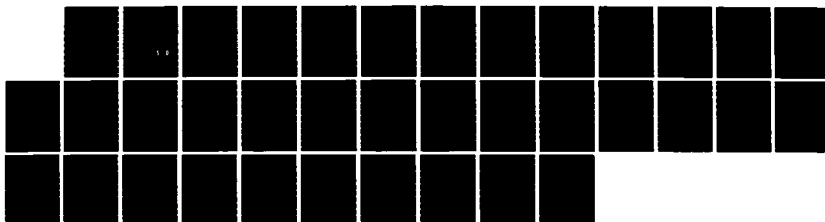
EXPANDABLE EPOXY APPLICATION(U) ATLANTIC RESEARCH CORP
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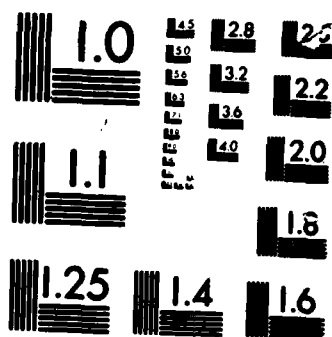
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TR-PL-11976

FIRST DRAFT
FINAL REPORT

EXPANDABLE EPOXY APPLICATION

T. F. Davidson
G. Rogowski

Contract No. DASG60-84-C-0112

April 25, 1986

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FINAL REPORT

EXPANDABLE EPOXY APPLICATION

**T. F. Davidson
G. Rogowski**

Contract No. DASG60-84-C-0112

Submitted by:

**ATLANTIC RESEARCH CORPORATION
7511 Wellington Road
Gainesville, VA 22065**

April 25, 1986

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1.0 INTRODUCTION

→Epoxy resins are widely used throughout the industry as the matrix in structural composites. Epoxides undergo the least amount of shrinkage during cure of the available composite matrices. However, this shrinkage, which is usually around 5 percent does affect a reduction in the performance of the composite. This reduction in performance can be the result of poor adhesion between the matrix and the reinforcing fibers or the formation of stress concentrations in the matrix due to the presence of microcracks, both of which lead to the failure of the composite.

Cyclic monomers which undergo expansion during a cationic ring opening polymerization have the potential of reducing or eliminating the shrinkage that occurs in epoxy resins. The expansion of the monomers during the polymerization process is due to the transformation of covalent bonds in the monomer ring to Van der Waals type interactions with the formation of the polymer. This expansion can also occur if the cyclic monomers are copolymerized with an epoxy, thus reducing or eliminating the shrinkage. The cyclic monomer chosen for this program was 3,9-bis (5'-norbornene-2'-yl) -1,5,7,11-tetraoxaspiro 5,5 undecane which showed the most promise in preliminary studies.

2.0 OBJECTIVE

The objectives of this program are ~~threefold~~: 1) to evaluate the effects of incorporating limited percentages of the bisspiro orthocarbonate in epoxy resins; 2) To determine the improvements in subscale composite motor cases using a bisspiro/epoxy resin; ^{and} 3) To determine the merit of fabricating pressure bottles using a layered procedure for their construction.

3.0 SUMMARY

This section will be completed for the final draft-camera ready copy. It has not been included here since the final evaluation (pressure testing the fabricated bottles) has not been completed.

4.0 EXPERIMENTAL RESULTS

4.1 RESIN EVALUATION

4.1.1 BASELINE/BISSPIRO RESIN EVALUATION

Four different levels of bispiro (15,20,25,35) were evaluated in the initial baseline resin system which consisted of EPON 828, EPON 871, TONOX 60/40 and diglycidyl ether. A latent catalyst (XU-213) was used to promote the copolymerization of the bispiro and epoxy resin. Three different levels of bispiro were tried in the initial formulations as well as two different cure cycles. These formulations are given in Table 1. The resins were mixed by first blending EPON 828 and EPON 871 followed by the addition of the bispiro, TONOX 60/40, and finally the XU-213. Aluminum dishes were used to prepare cured samples for qualitative evaluation. Analysis of the cured samples indicated that the bispiro had not polymerized and had settled to the bottom of the cure cup during cure. These same formulations were tried a second time using a different mixing procedure. After the EPON 828 and 871 were blended, the bispiro was added and a mortar and pestle was used to mix the resin. The mixing procedure substantially improved the resin/bispiro dispersion. The resins were then cured using the two different cure cycles and the same results were obtained as with the previous samples.

4.1.2 ALTERNATE CURATIVE EVALUATION

Alternate curatives and catalysts were evaluated in the initial baseline resin in an attempt to eliminate the phase separation that was occurring when the resins were cured. The formulations for these resins are given in Table 2. The alternate curatives that were evaluated included

Table 1. Baseline Resins/Bissspiro Compatibility

● RESIN FORMULATIONS:

INGREDIENTS	PARTS /100PARTS RESIN			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
EPON 828	50	50	50	50
EPON 871	50	50	50	50
DIGLYCIDYL ETHER	25	25	25	25
TONOX 60/40	20	20	20	20
XU-213	-	1.0	2.0	4.0
BISSPIRO	-	15	15	15
CURE CYCLE*	1	1, 2	1, 2	1, 2

*CURE CYCLES: 1: 4 HOURS @ 100°C

1 HOUR @ 150°C

2: 4 HOURS @ 60°C

1 HOUR @ 150°C

orthophenylenediamine (OPDA), 2,6-diaminopyridine (DAP), and Curing Agent Y from Shell. Several anhydrides were also evaluated based on a recommendation from the BMDATC. These were as follows:

Nadic Methyl Anhydride (NMA)

Hexahydrophthalic Anhydride (HHPA)

Tetrahydrophthalic Anhydride (THPA)

Dodecenylsuccinic Anhydride (DDSA)

Chlorendic Anhydride (HET)

Phthalic Anhydride (PA)

Pyromellitic Dianhydride (PMDA)

In addition to the curatives, several alternate catalysts were evaluated in place of the XU-213. These were also Lewis acid catalysts based on boron trifluoride instead of boron trichloride 6 found in XU-213. These catalysts were as follows:

Boron Trifluoride Orthophenylenediamine (BF_3 OPDA)

Boron Trifluoride Monoethylamine (BF_3 MEA)

Boron Trifluoride Piperidine (BF_3 Piperidine)

Boron Trifluoride Aniline (BF_3 Aniline)

Several different cure cycles were also tried with these formulations in order to vary the rates of polymerization of the bispiro and epoxy. Post cures were kept the same because most of the polymerization between the bispiro and epoxy takes place during the initial part of the cure. These cure cycles are also given in Table 2.

Aluminum disks were again used as cure cups to determine the characteristics of the cured resin. Each cure cup was dissected to determine if layers were formed during the cure cycle. The results of the study indicated that all of the resins evaluated, including the baseline with the bispiro,

Table 2. Baseline Resin/Bispiro/Alternate Curatives Evaluation

	PARTS/100 PARTS RESIN						
	<u>5</u>	<u>6</u>	<u>7</u>	<u>8</u>	<u>9</u>	<u>10</u>	<u>11</u>
EPON 828	50	50	50	50	50	50	50
EPON 871	50	50	50	50	50	50	50
DIGLYCIDYL ETHER	25	25	25	25	25	25	25
TONOX 60/40	20	-	-	-	-	-	-
BISSPIRO	15	15	15	15	15	15	15
OPDA	10	20	20	20	-	-	-
2, 6 DAP	-	-	-	-	20	20	20
XU-213	2.0	-	-	-	2.0	-	-
BF3 OPDA	-	5.0	-	-	-	5.0	-
BF3 MEA	-	-	2.0	-	-	-	2.0
BF3 PIPERIDINE	-	-	-	2.0	-	-	-
CURE CYCLE*	2, 3	1, 3	2, 3	1, 2	1, 3	2, 3	1, 2

*CURE CYCLE: 1: 4 HRS. @ 100°C; 1 HR. @ 150°C

2: 4 HRS. @ 80°C; 1 HR. @ 150°C

3: 4 HRS. @ 60°C; 1 HR. @ 150°C

Table 2. (Continued)

FORMULATIONS (CONT'D)

	PARTS/100 PARTS RESIN							
	<u>12</u>	<u>13</u>	<u>14</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>	
EPON 828	50	50	50	50	50	50	50	
EPON 871	50	50	50	50	50	50	50	
ETHER	25	25	25	25	25	25	25	
BISSPIRO	15	15	15	15	15	15	15	
2,6 DAP	20	-	-	-	-	-	-	
CURING AGENT Y	-	30	30	30	30	-	-	
H 906	-	-	-	-	-	80	80	
XU 213	-	2.0	-	-	-	2.0	4.0	
BF3 OPDA	-	-	5.0	-	-	-	-	
BF3 MEA	-	-	-	2.0	-	-	-	
BF3 PIPERIDINE	-	-	-	-	2.0	-	-	
BF3 ANILINE	2.0	-	-	-	-	-	-	
DMP 30	-	-	-	-	-	2.0	2.0	
CURE CYCLE*	2, 3	1	1	1	1	1	1	
<hr/>								
*CURE CYCLES:	1:	4 HRS. @ 100°C	2:	4 HRS. @ 80°C	3:	4 HRS. @ 60°C		
		1 HR. @ 150°C		1 HR. @ 150°C		1 HR. @ 150°C		

Table 2. (Continued)

FORMULATIONS (CONT'D)	PARTS/100 PARTS RESIN						
	19	20	21	22	23	24	25
EPON 828	50						▲
EPON 871	50						▲
ETHER	25						▲
BISSPIRO	15						▲
XU-213	1						▲
NMA	80	--	--	--	--	--	--
DDSA	--	130	--	--	--	--	--
CA (HET)	--	--	100	--	--	--	--
HHPA	--	--	--	--	--	--	75
THPA	--	--	--	75	--	--	--
PA	--	--	--	--	75	--	--
PMDA	--	--	--	--	--	75	--

CURE TIME: 4 HOURS @ 150°C

had developed two distinct layers in the cured resin, the bottom layer consisted of polymerized bispiro as well as overreacted bispiro. This layer varied in thickness from 10-15 mil. The top layer, which was the thickest layer, contained the cross-linked epoxy resin. It was not possible to determine if any of the bispiro had actually copolymerized with the epoxy resin. In addition, the variation of the cure rates did not eliminate the formation of the two layers.

The anhydride cured resins were accelerated with XU-213 (BCl_3 -amine complex) and cured at 150°C for four hours. All of the resins reached an adequate state of cure; however, the characteristics of the cured state were drastically different for each formulation. Formulations 19 and 20 produced two distinct layers in the cure cups with the top layer consisting of the 828/871 resin and the bottom layer predominantly bispiro monomer. Both formulations exhibited a small amount of shrinkage on cure since both systems contracted away from the aluminum cure cups when cooled to temperature. Formulation 24, which was cured with PMDA, exhibited the most homogeneous cure. The bispiro in this formulation appeared to have polymerized to a certain extent since no bispiro monomer was present in the bottom of the cure cup. It appears that shrinkage of this resin also occurred since the cured resin was easily removed from the aluminum dish. This might be an indication that a larger concentration of the bispiro is needed to eliminate the shrinkage in this formulation. The cure characteristics of this resin were by far the best obtained to date with the EPON 828/EPON 871 system. The final four formulations, 21, 22, 23 and 25, exhibited a very exothermic cure since a large number of voids were obtained in each formulation. There was still evidence of unreacted bispiro in all four formulations indicating that the

anhydrides used in these formulations did not aid in the polymerization of the bispiro.

The results of anhydride curative evaluation indicated that the slower reaction rates obtained with most of the anhydrides improved the characteristics of the cured resin. However, several formulations still possessed unreacted bispiro monomer in the cured resin. Only in one formulation (24) did it appear that the bispiro had undergone some type of polymerization. This result is questionable since one would expect some type of expansion to take place, if indeed the bispiro had polymerized. The mechanism of cross-linking of the epoxy resin might be another reason why improvements in the cured resins were obtained with the anhydrides. The cross-linking occurs primarily through the hydroxyl groups when an anhydride is used as the curative. This is in contrast to polyamine curatives evaluated in previous studies where cross-linking involves the base-catalyzed opening of the epoxide groups.

4.1.3 ALTERNATE BASELINE RESINS

Two alternate epoxies were evaluated to determine if the bispiro might be more compatible and therefore copolymerize with the epoxy during cure. The first epoxy tried was MY-720 from Ciba-Geigy. MY-720 is a multifunctional epoxy resin obtained by reacting methylene dianiline with epichlorohydrin. When cured with an anhydride, a three-dimensional high density cross linked network is obtained which has exceptional heat and chemical resistance.

The formulations for the resins evaluated with bispiro are given in Table 3. The bispiro concentration remained constant at 10 percent for all three resins. The only difference in the three formulations was the concentration of the latent catalyst, XU-213 (BCl_3 -amine complex), which was varied

from 0.5-2.0 parts per hundred resin. Two different cure cycles were used to vary the reaction rates of the monomers. The results obtained with these formulations were again similar to the results obtained with the baseline resin system. A thin layer of unreacted bisspiro was still present at the bottom of each cure cup, indicating that a substantial percentage of the bisspiro was not copolymerizing with the epoxy. Due to these results, no further testing of this resin was conducted.

Table 3. MY-720/BISSPIRO FORMULATIONS.

<u>Ingredients</u>	<u>Parts/100 Parts Resin</u>		
	<u>1</u>	<u>2</u>	<u>3</u>
Araldite MY-720	100	100	100
Hardener 906 (anhydride)	110	100	100
Bisspiro	22	22	22
XU-213	0.5	1.0	2.0

Cure Cycles: 1 - 2 hours @ 100°C

3 hours @ 180°C

2 - 4 hours @ 80°C

6 hours @ 150°C

The second epoxy resin system tried was Shell's EPON 9400/9450 which is a conventional bisphenol A epichlorohydrin resin which has been modified with styrene.

The formulation for the resins evaluated are given in Table 4. In the first two formulations, the bisspiro level remained the same at 15 percent by weight, and the accelerator type was changed to determine the effect of the accelerator on the copolymerization of the bisspiro and epoxy. The bisspiro

particle size was reduced to approximately 120 microns using a ceramic ball-mill prior to incorporation in all of the formulations. This greatly improved the quality of the bispiro/epoxy dispersion as well as the stability. Both formulation 1 and 2 cured homogeneously using the cure conditions given in Table 4. Thermal analysis was run on the two samples to determine the extent of the copolymerization of the epoxy and the bispiro. This involved the determination of the glass transition temperatures using DSC and the decomposition temperatures using TGA. The DSC and TGA curves for both formulations are given in Figures 1-4.

The Tg for the XU-213 accelerated system was determined to be 127.0°C (Figure 1), whereas the Tg for the RSM-604 accelerated system was somewhat lower at 114.7°C (Figure 3). This suggests that the XU-213 is possibly a more efficient accelerator for the bispiro/9400 system than RSM-604 which was formulated specifically for the 9400/9450 system. The DSC curves also indicate that only one material is present in both cured resins since only one glass transition temperature was observed for each resin. This is a good indication that the bispiro entered into the copolymerization with the epoxy leaving no unreacted bispiro.

In order to interpret the TGA curves for formulations 1 and 2, a small study was conducted on the bispiro monomer. In this study, the bispiro was homopolymerized using XU-213. This was accomplished by mixing 3.0g of bispiro monomer with 0.2g of the XU-213 and heating this mixture at 150°C for 5 hours. The resultant product was a hard, red-glassy polymer. A TGA was then run on this sample (Figure 6) and compared to the TGA of the bispiro monomer (Figure 5). A comparison of the TGA curves indicated that the bispiro had indeed polymerized using XU-213 and that the decomposition temperature was increased from 145.9°C to 251.7°C. These curves were then

Sample: EXP POLMR ORTHO #1

Size: 11.50MG AMB HERM

Rate: 20 C/MIN N2

Program: General Analysis V1.0

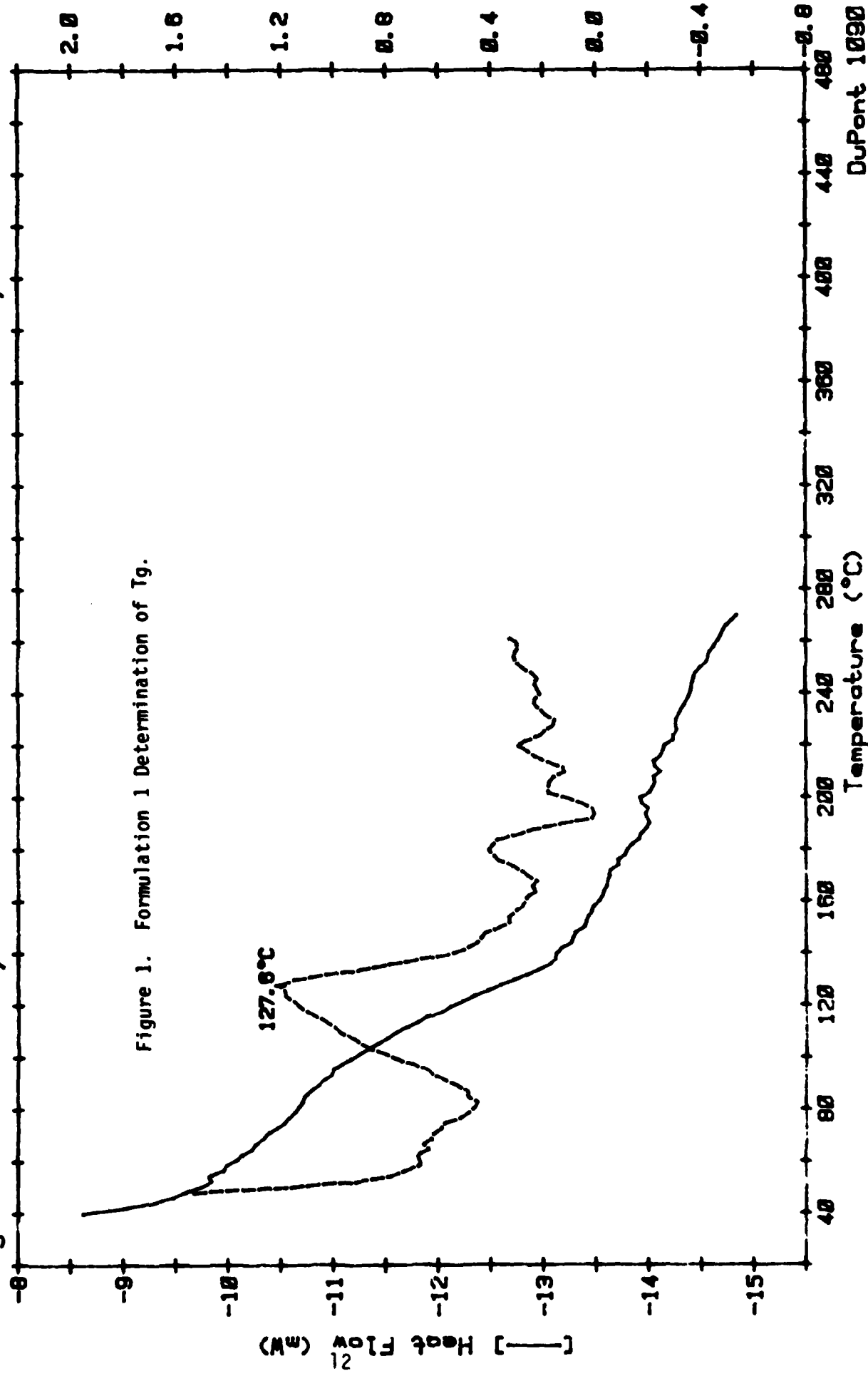
DSC

Date: 24-May-85 Time: 12:00:56

File: EXPLMOR#1.04 ARC DSC #36

Operator: CTS

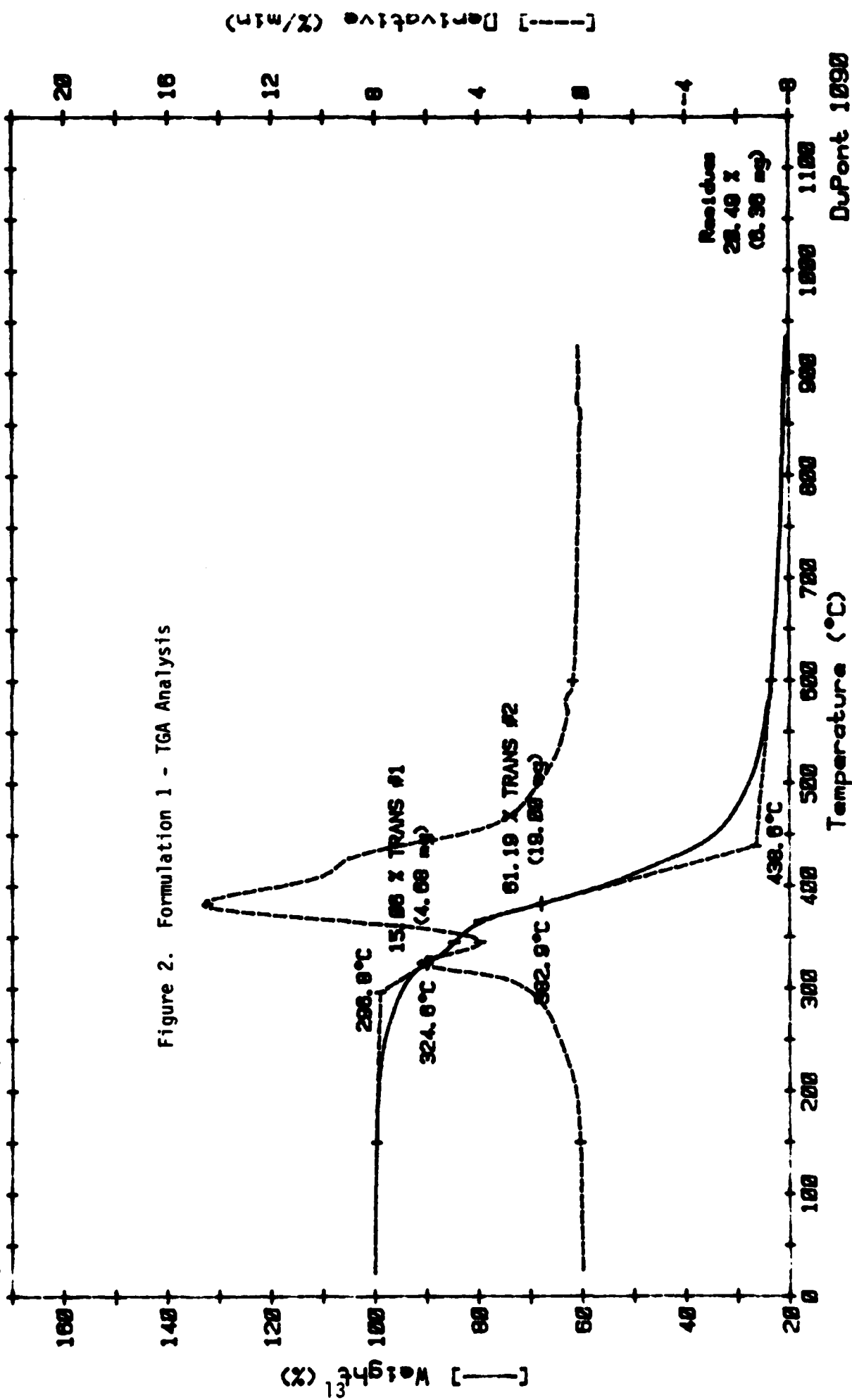
Plotted: 24-May-85 12:19:12



Samples: EXP POLR ORTHO #1
 Size: 31.05 mg
 Rate: 20 C/MIN N2
 Program: TGA Analysis V2.0

TGA

Date: 28-May-85 Times: 9:36:33
 File: EXPLMRORT1.01 ARC TGA#7
 Operator: CTS
 Plotted: 28-May-85 10:37:16



DATE: 24-MAY-85 TIME: 13:36:05 FILE: EXPLMOR#2.02 ARC DSC #36 OPERATOR: CTS PLOTTED: 24-MAY-85 13:52:01

SAMPLE: EXP POLMR ORTHO #2

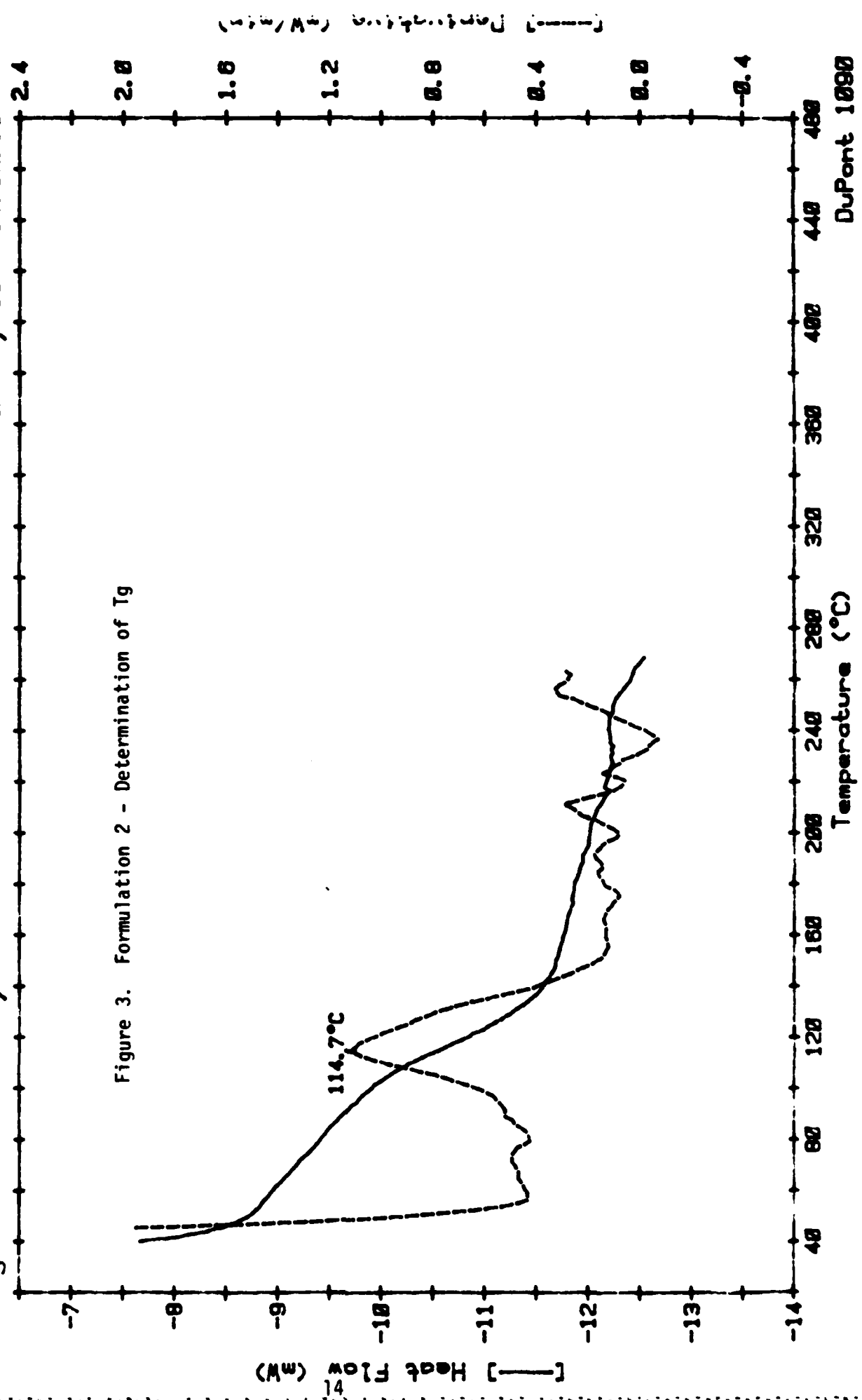
SIZE: 9.25MG AMB HERM

RATE: 20 C/MIN N2

PROGRAM: General Analysis V1.0

DSC

Figure 3. Formulation 2 - Determination of Tg



Sample: EXP POLMR ORTHO #2

Size: 31.47 mg

Rate: 20 C/MIN N2

Program: TGA Analysis V2.0

TGA

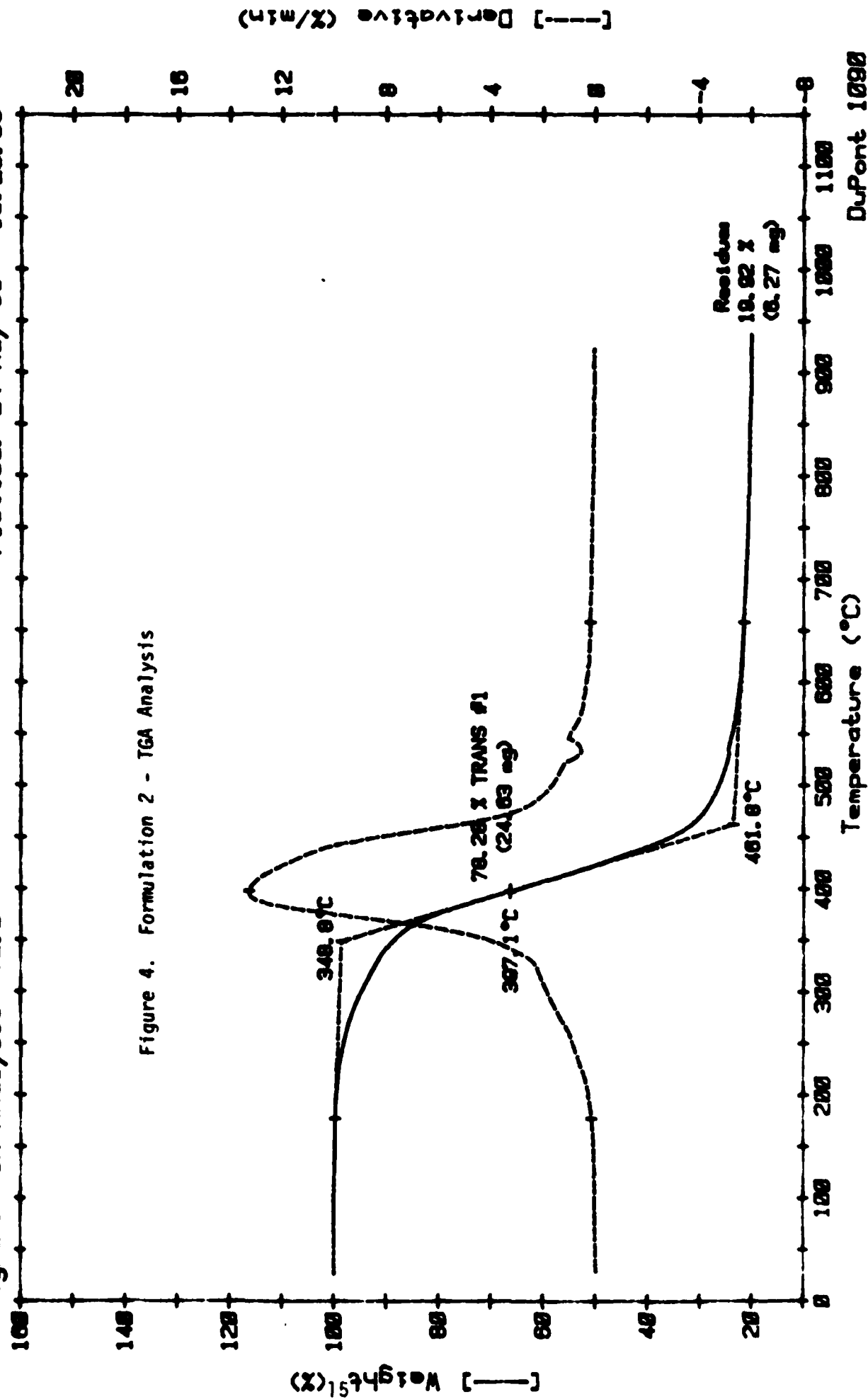
Date: 24-May-85 Time: 14:23:07

File: EXPLMOR#2.01 ARC TGA#7

Operator: CTS

Plotted: 24-May-85 15:28:38

Figure 4. Formulation 2 - TGA Analysis



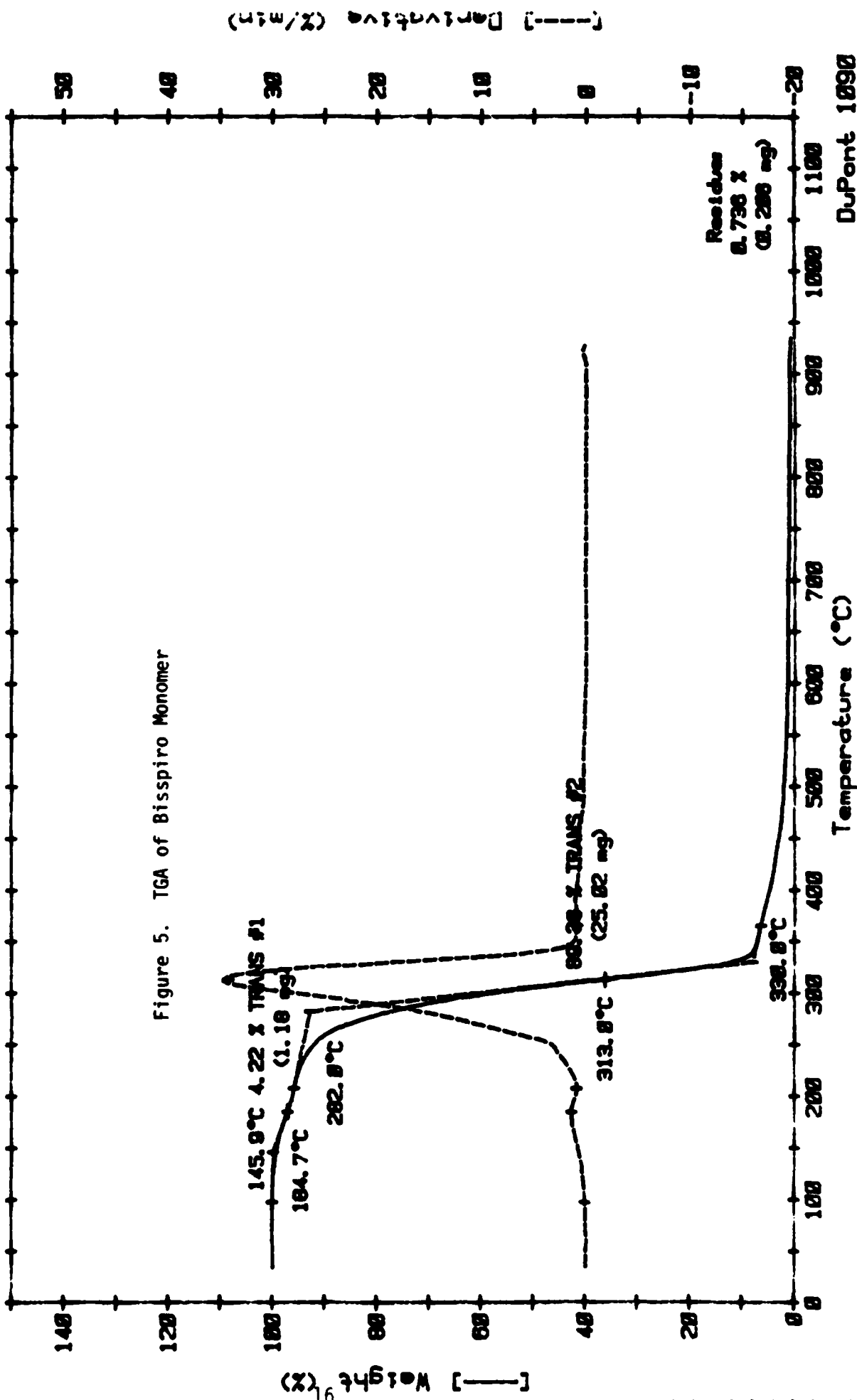
Temperature (°C)

DuPont 1090B

Samples: EXP POLR BISSPIRO
 Size: 28.00 mg
 Rate: 20 C/MIN N2
 Program: TGA Analysis V2.0

TGA

Date: 28-May-85 Time: 11:24:50
 File: EXPLMRBISP.01 ARC TGA#7
 Operator: CTS
 Plotted: 28-May-85 12:16:11



Sample: EXP PLMR BISSPOLYMER

Size: 22.55 mg

Rate: 20 C/MIN N2

Program: TGA Analysis V2.0

TGA

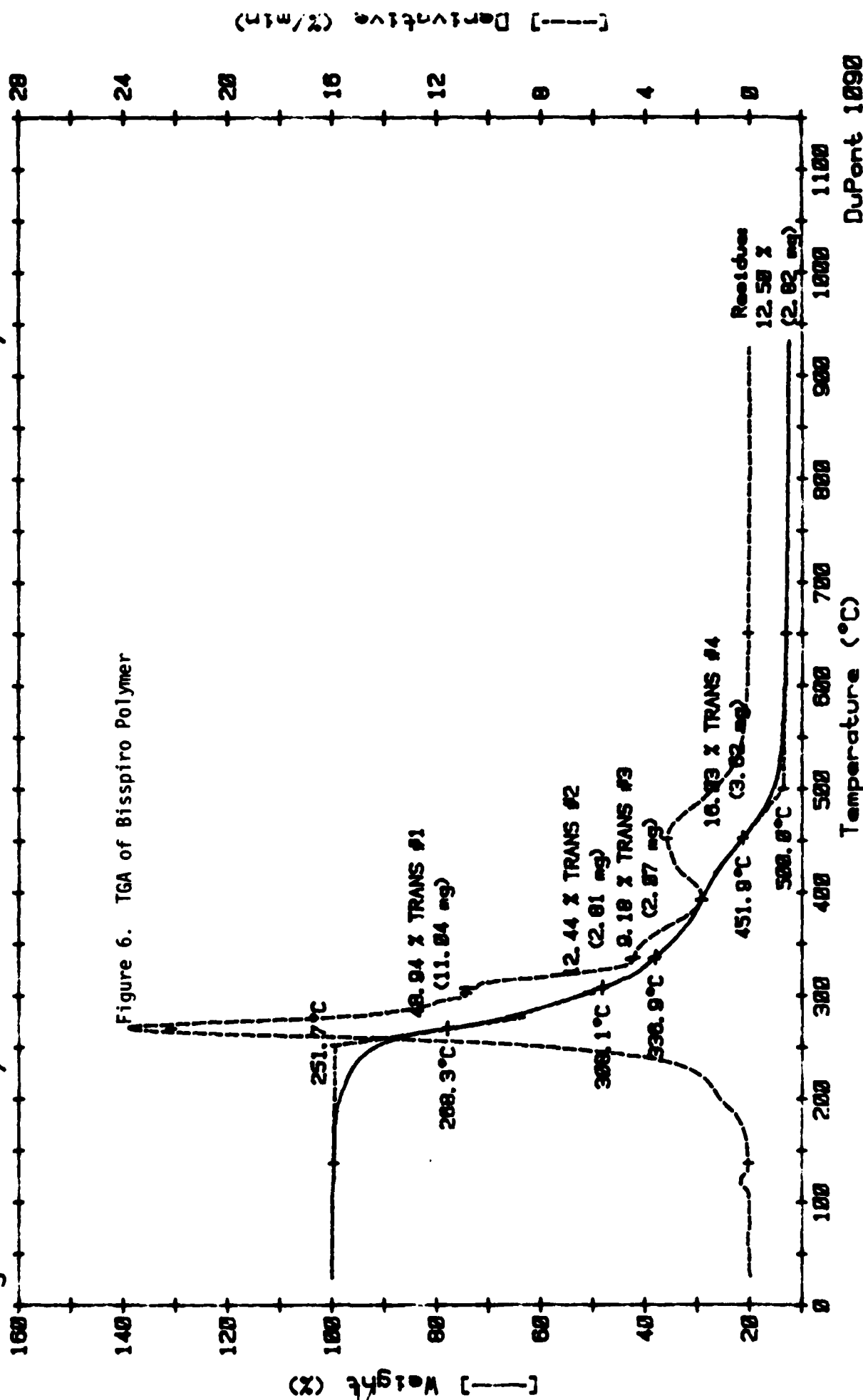
Date: 28-May-85

Time: 13:46:21

File: EXPLMRBISS.01 ARC TGA#7

Operator: CTS

Plotted: 28-May-85 14:42:27



used as comparison for the TGA curves obtained with formulations 1 and 2. The decomposition temperatures for formulations 1 and 2 were 296.8°C and 348.8°, respectively, both of which were higher than the decomposition temperatures obtained with the bispiro monomer and polymer. This data further substantiates the copolymerization of the bispiro and the epoxy since a two-phase decomposition was not observed and the decomposition temperature of the resins were well above the bispiro decomposition temperatures. In addition, the results of the TGA also suggest that the predominant polymerization was between the epoxy and the bispiro and not the homopolymerization of the bispiro since the decomposition temperatures of the resins and the bispiro polymer were different.

Different levels of bispiro were also investigated with the 9400/9450 system. The formulations are given in Table 4. The levels of bispiro that were evaluated were 20, 25, and 30 percent by weight. The accelerator used for this evaluation was XU-213 at a level of 1.5 phr. All three formulations were cured for 1 hour at 100°C, followed by 4 hours at 150°C. The analysis of the cure cups indicated a homogeneous cure for all three levels of bispiro.

Further testing of the 9400/9450 resin system was justified based on the excellent results obtained with the cure cups which indicated a homogeneous cure. Pot life studies were run on the 9400/9450 control, as well as 15, 20, 25 and 35 percent bispiro levels in 9400. These formulations are given in Table 5. The results of the pot life study are given in Figure 7. The 15, 20, and 25 percent levels of bispiro had adequate pot life for utilization in the filament winding operation. However, the 35 percent level of bispiro became too viscous to be used effectively during the winding process. Based

Table 4. EPON 9400/9450 Bispiro Formulations

<u>Ingredients, phr</u>	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>	<u>5</u>
EPON 9400	100	100	100	100	100
EPON 9450	31.5	31.5	31.5	31.5	31.5
Bispiro	23.0	23.0	33.0	45.0	57.0
XU-213	1.5	--	1.5	1.5	1.5
RSM-604	--	1.5	--	--	--
(% Bispiro)	(15)	(15)	(20)	(25)	(30)
Cure Conditions	1 hr. @ 100°C	--- 1 hr. @ 100°C---			
	1 hr. @ 150°C	--- 4 hr. @ 150°C---			

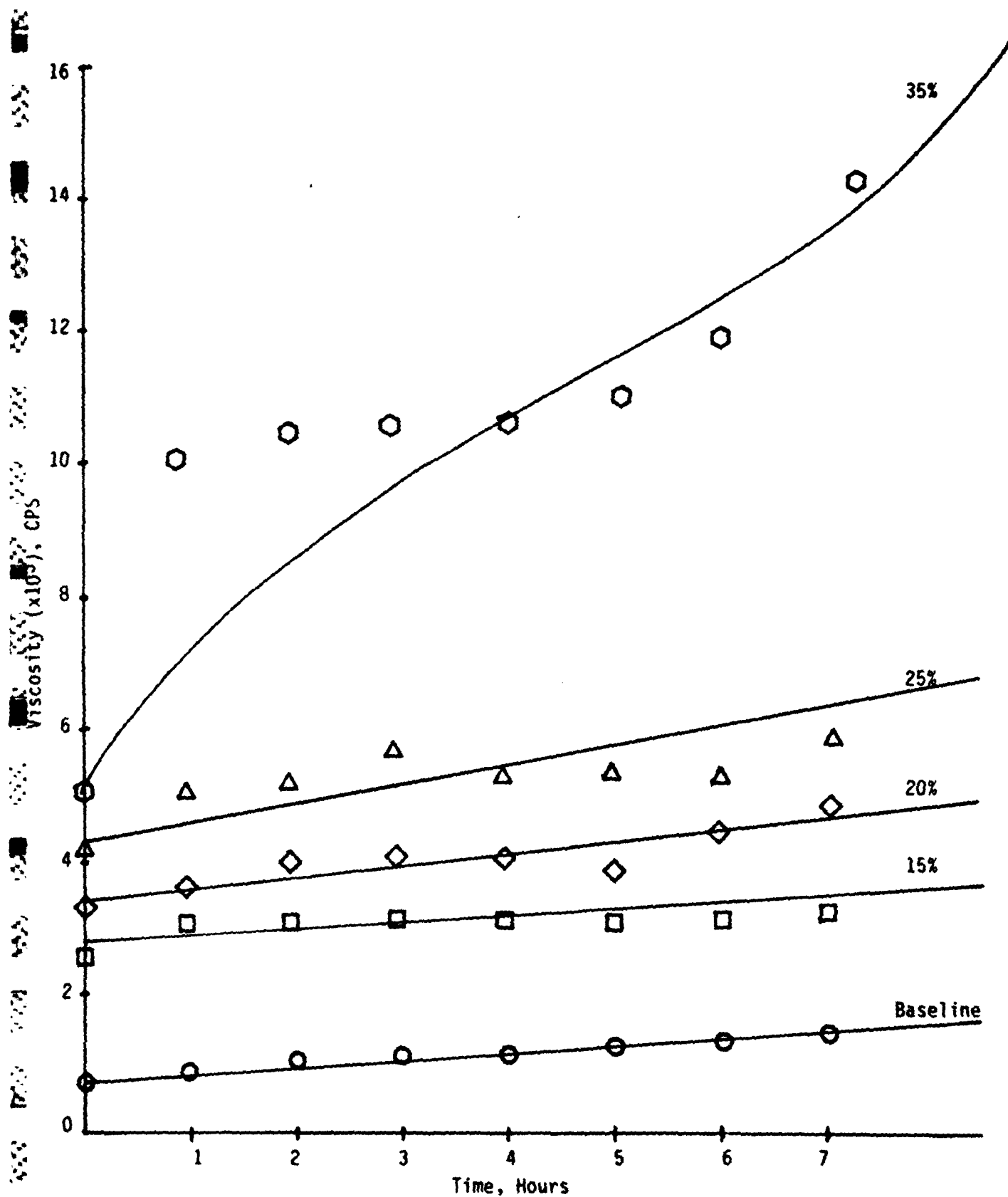


Figure 7. Room Temperature Pot Life of Various Bisspiro Resins (Brookfield Viscosity)

Table 5. Bisspiro/9400/9450 Formulations

<u>INGREDIENTS*</u>	<u>PARTS/HUNDRED PARTS RESIN</u>				
	<u>BASELINE</u>	<u>15%</u>	<u>20%</u>	<u>25%</u>	<u>35%</u>
EPON 9400	100	100	100	100	100
EPON 9450	31.5	36	36	36	36
PC-1344	0.47	0.47	0.47	0.47	0.47
XU-213	--	1.5	1.5	1.5	1.5
BISSPIRO	--	29.5	34.0	46.0	73.5

on this information the 35-percent level was eliminated from any further testing.

Shrinkage measurements were also determined for the different levels of bispiro as well as the 9400/9450 control. The results are outlined below:

EPON 9400 (PHR)	EPON 9450 (PHR)	PC-1344 (PHR)	XU-213 (PHR)	BISSPIRO (PHR)	CURE SHRINKAGE (PERCENT)
100	31.5	0.47	--	--	6.00
100	36	0.47	1.5	29.5	2.91
100	36	0.47	1.5	34.0	1.60
100	36	0.47	1.5	46.0	1.74

The shrinkage measurements were determined by comparing the uncured densities with the cured densities. Initial problems were encountered with voids in the cured samples due to inadequate degassing of the uncured resin. The presence of voids produced artificially low shrinkage results with all three levels of bispiro. In order to facilitate the degassing of the uncured resin, a defoamer (PC-1344) was incorporated in each resin, including the control. The use of the defoamer substantially improved the quality of the cured samples, providing a void-free resin for density determinations and accurate shrinkage results.

The results of the shrinkage measurements indicate that expansion is taking place with all three levels of bispiro. The lowest shrinkage was obtained with 20 percent bispiro. It appears from the data that the reduction in shrinkage reaches a peak with 20% bispiro, and no further improvement is noticed with increasing levels of bispiro. Based on these results, the 20 percent bispiro resin was selected for comparison to the baseline resin and layered construction for the 6-inch diameter cylindrical pressure bottles.

4.2 Phase 2 - Composite Parts Manufacture

4.2.1 NORMAL AND LAYERED MANUFACTURE

4.2.1.1 MANUFACTURING DISCUSSION

After determining the proper epoxy resin system, compatible curatives, and accelerating additives; the following materials were fabricated.

First, unidirectional Kevlar and graphite flat panels were fabricated with 9400/9450 baseline resin as well as the 15 percent, 20 percent, and 25 percent bispiro resin. The fabrication process consisted of hoop winding 0.007-inch thick plies at an 89° angle on a rectangular cross-section mandrel. The correct number of plies were wound to yield the desired panel thickness, i.e., 0.035-inch for tensile panels and 0.125-inch for shear panels. After the completion of winding, the fibers were trapped between caul plates, the excess fiber trimmed away, and the panels removed from the mandrel. the panels were bagged and press cured at 100 psi for the specified cure cycles.

Tensile and short beam shear specimens were prepared from the different panels with the exception of the 20 percent bispiro where only shear specimens were prepared from it. In order to evaluate the tensile and shear behavior, ARC fabricated and tested five tensile and short beam shear samples from each resin and fiber system. Stress-strain curves, tensile ultimate and modulus, and shear ultimate and modulus were obtained for each specimen and statistically evaluated.

Second, design verifications for the ASTM six-inch pressure vessels were carried out by hydrobursting two preliminary vessels. This was done to verify the optimum number of hoops and helicals as well as their arrangement within the bottle. Two 5.75-inch FIA pressure bottles were wound under IR&D funds with Shell 9400/9450 epoxy resin and Hercules IM6 graphite fiber. The mandrels were coated with rubber liners prior to winding in order to form internal bladders which were left intact for the burst testing.

Third, eighteen ASTM six-inch diameter, cylindrical pressure bottles were fabricated; six baseline, six bispiro, and six layered. All bottles were fabricated using Hercules IM6 graphite and the same winding configuration. The baseline bottles used the shell 9400/9450 epoxy resin system. The bispiro bottles used the shell 9400/9450 epoxy resin system with 20 percent bispiro by weight added to it. The layered bottles used four epoxy resin systems based around shell 9400/9450 with varying modulus. The resin mix ratios and corresponding modulus values are listed below.

	<u>PARTS/HUNDRED PARTS RESIN</u>			
	<u>1</u>	<u>2</u>	<u>3</u>	<u>4</u>
EPON 9400	25	50	75	100
RSL-960	75	50	25	---
EPON 9450	32.5	33.7	34.3	31.5
RSM-604	1.0	1.0	1.0	---
MODULUS, KSI	150	250	350	450

The four resin systems were dispersed throughout the wind in layers as follows:

Layer #1 1st Helical

Layer #2 1st Hoop

Layer #3 2nd Helical

Layer #4 2nd and 3rd Hoops

The winding configuration was 1 helical layer - 1 hoop layer - 1 helical layer 2 hoop layers. The helical-to-hoop stress ratio was 0.80 based on netting analysis. Other design and manufacturing data are shown below.

	<u>Helicals</u>	<u>Hoops</u>
Fiber Angle	16.0°	89.0°
# of Layers	2	3
Thickness of Layer	0.014	0.014
Band Width	.3	.3
# of Spools	3	3
Winding Tension	± .2 lb/tow	2 ± .2 lb/tow

During fabrication processing problems were encountered in bonding the silicone rubber bladder to the metallic polar bosses and in preventing gas bubbles in the bladder. The supplier of the silicone to metal primer, D-Aircraft, apparently recommended the wrong primer, Dapco 1-200. A new primer, Dapco 1-100, was ordered from D-Aircraft after discussions with them concerning the problems ARC was having in obtaining a good bond between the silicone rubber and the metallic polar bosses. Upon receiving the new primer, several bond studies were conducted. The resultant bonds were good, indicating that the poor bonds obtained with the previous primer were due to the incorrect primer. In addressing the bubbles in the bladder, a change was made from using a screenable thixotropic silicone rubber, Dapcicast 62, to a calendared "B staged" silicone, SMC 1050. This eliminated the folding in of air bubbles during the screening operation which would expand during cure yielding an unsatisfactory bladder. With the correction of these problems, the bottles were wound without any further incidents.

4.2.1.2 CASE CURE CYCLES

The cure steps are listed below for the baseline and layered bottles. Cure:

- 1) Rotated and staged in an electric oven 1/2-hour at 170°F.
- 2) Two hours at 300°F in a gas-fired oven.

The cure steps are listed below for the 20 percent bispiro bottles. The bottles were continuously rotated in an electric oven throughout the cure cycle.

- Cure:
- 1) 1 hour at 176°F
 - 2) 1 hour at 248°F
 - 3) 1 hour at 302°F
 - 4) 1 hour at 347°F.

Test data is located in Section 4.2.3.

4.2.2 TESTING

4.2.2.1 SAMPLE PREPARATION

Specimens for tensile properties evaluation were prepared from cured panels for each of the 9400/9450 control, 15 percent and 25 percent bispiro levels for both graphite and Kevlar systems to conform to ASTM D3039 standards. Panels were 12-inch length x 10-inch width x .030-inch thickness.

4.2.2.2 GRAPHITE SPECIMEN PREPARATION

Graphite specimens were prepared by first rough cutting, then squaring, marking and aligning the panel to final dimensions (8-inch length x 9-inch width). Panel is then cut to a rectangular shape. All cutting of graphite panels and specimens was performed using a diamond grit blade on a radial saw. After cutting, the panels were sanded in the tab-end regions using medium-grit silicon carbide paper. After sanding, panels were solvent wiped and allowed to air dry. Fiberglass (NEMA grade) end tab strips were then applied using EA-934 adhesive, a two-part epoxy system. Panel and end tabs are then placed into an alignment mold and clamps or weights applied during the curing process. After cure, panels are removed from mold and specimens cut to 0.5-inch widths. Specimens are then examined for flaws and measured for thickness, width, and length.

Initial testing of the 9400/9450 graphite control samples was performed using a DSST (Measurements Technology, Inc.) extensometer for measurement of strain properties. However, it was found that the extensometer was slightly in error and also slipped during testing of the samples. Therefore, it was decided to use bonded strain gages for the remaining tests at all bispiro levels for both graphite and Kevlar materials. Strain gages (Micro-measurements, Div. of Measurements Group, Inc., Gage No. CEA-00-1870W-350) were then bonded to the graphite specimens using the appropriate surface preparation techniques and adhesive recommended by the gage manufacturer. Lead wires were soldered to the gage terminals, thus concluding the preparation process.

4.2.2.3 KEVLAR SPECIMEN PREPARATION

Kevlar panel and specimen dimensions were the same as those for the graphite systems. However, due to the softer, fibrous nature of the aramid fibers, different cutting and machining methods were used to prevent "fuzzing" when cutting in the longitudinal (with fiberglass) direction or "brooming" when cutting in the transverse (across the fiber grain) direction. Also, machining is performed without end tab strips applied since the methods followed preclude the cutting of three dissimilar materials (Kevlar, fiberglass, and adhesive) simultaneously. The Kevlar panels are first rough cut into strips using a bandsaw fitted with an intermittently toothed silicon carbide blade. To prevent fibers "loading up" on the blade, it is periodically cleaned between cuts. Rough strips are then sandwiched between 1/16-inch thick aluminum plates and final longitudinal tensile dimensions machined using a carbide-tipped flycutter on a Bridgeport mill. Cross grain cuts are performed using a specially modified carbide-tipped blade. End tabs of fiberglass material were then applied to each individual specimen using the EA-934 adhesive, assemblies placed into a mold, weights applied and allowed to

cure. After cure specimens were examined and measurements of thickness, width, and length recorded. Strain gages and application techniques used for the Kevlar specimens were identical to those used for the graphite specimens with one exception. Since Kevlar fuzzes immediately on sanding, no sanding or roughening operation was used prior to the gage installation. Extra care was taken, however, in the cleaning and conditioner and neutralizer applications to assure an optimum bond was achieved. We encountered no gage unbond problems when these specimens were tested.

Tensile tests for both Kevlar and graphite systems were performed on an MTS Model 810 servohydraulic tester at a crosshead rate of 0.05 in/min. Strain gage readings were routed through a Vishay signal conditioner and output to Hewlett Packard recorders. Load cell output from the load cell amplifier circuits were also output to the same recorders, thus providing traces of load (lbs) versus deflection (microstrain, ϵ) for each specimen. At least five specimens were tested for each resin system and fiber material; however, a number of specimens failed at the tab ends. Tests resulting in tab failures were considered invalid.

Tensile results are shown in Tables 6 and 7.

Overall, experimental tensile properties were in good agreement with theoretical properties for the baseline data. It also appears that bispiro levels did not significantly effect the graphite properties. Significant decreases in both strength and modulus were observed at the 15 percent bispiro level in the Kevlar specimens. A somewhat less reduction in strength occurred at the 25 percent level. Although there appears to be a trend in this data, no conclusions can be reached because the data is somewhat limited. Tensile properties are fiber dominated, therefore, there is no obvious theoretical mechanisms for this behavior. More data is needed to reach definitive conclusions.

Table 6. Graphite Tensile Specimens							
Resin System	Number of specimens	Stress (KSI)	C.V. (%)	Strain @ Failure (%)	C.V. (%)	Elastic Modulus (MSI)	C.V. (%)
Baseline	1	340.6	-	*		22.5	-
15% Bisspiro	4	332.3	3.2	1.4	3.5	24.9	1.9
25% Bisspiro	6	349.8	4.6	1.4	3.2	23.6	3.7

Table 7. Kevlar Tensile Specimens							
Resin System	Number of Specimens	Stress (KSI)	C.V. (%)	Strain @ Failure (%)	C.V. (%)	Elastic Modulus (MSI)	C.V. (%)
Baseline	2	220.3	-	1.75	-	12.7	-
15% Bisspiro	2	162.4	-	1.54	-	10.9	-
25% Bisspiro	4	184.1	5.7	1.69	10.0	11.4	2.8

*Unable to determine strain due to error in extensometer
C.V. Coefficient of Variation (Standard Deviation/Mean)

5.0 CONCLUSIONS

The following conclusions can be stated concerning the use of the expandable bispiro compound.

- 1) Of the resins evaluated, the best was the EPON 9400/9450 system.
- 2) The pot life resulting from this system are suitable for composite winding.
- 3) This resin/bispiro system is suitable for winding composite materials.
- 4) No mechanical property improvement was observed for plaques wound with the bispiro system over plaque without the bispiro system. This was presumably due to the fact that the mechanical properties are primarily controlled by the composite fibers.

6.0 RECOMMENDATIONS

- 1) Test designs which are more shear dominated in order to see full significance of the expanding resins.
- 2) Conduct damage tolerance tests.
- 3) Conduct additional resin work that will:
 - a. provide positive expansion with the bispiro-orthocarbonate polymer, and
 - b. determine if the expandable polymer can be used with resins developed by nations other than the U.S., i.e., Russian epoxies.

GLOSSARY

ARALDITE MY-720	N,N,N',N'-Tetraglycidyl-4,4'methylene-(bis)-aniline
BISSPIRO	3,9-Bis(5'-norborene-2'yl)-1,5,7,11-tetraoxaspiro 5,5 undecane
DAP	Diaminopyridine
DAPCO 1-100	Silicon to metal primer
DAPCO 1-200	Silicon to metal primer
DAPCOCAST 62	Silicone rubber material (paste)
DDSA	Dodecenylsuccinic Anhydride
DSC	Differential Scanning Calorimetry
EPON 828	Derivative of Bisphenol A-diglycidylether
EPON 871	Derivative of Bisphenol A-diglycidylether
EPON 9400	4,4'-Bisphenol A
EPON 9450	Epichlorohydrin and MDA
HARDENER 906	Nadic Methyl Anhydride
HET	Chlorendic Anhydride
HPHA	Hexahydrophthalic Anhydride
MEA	Monoethylamine
MY-720	Epoxyresin from methylene dianiline
NMA	Nadic Methyl Anhydride
PA	Phthalic Anhydride
PC-1344	Defoamer
phr	Parts per hundred parts of resin
PMDA	Pyromellitic Dianhydride
OPDA	Orthophenylenediamine
RSM-604	Catalyst

SHELL CURING AGENT Y	Aromatic amine
SMC 1050	Silicone rubber material (sheet)
Tg	Glass transition temperature
TGA	Thermal Gravimetric Analysis
THPA	Tetrahydrophthalic Anhydride
TONOX 60/40	Mixture: 65% 4,4'-diaminodiphenylmethane, 10% triamines, 25% polyamines
Xu-213	Boron Trichloride amine complex

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